SMALL ATOM DIFFUSION AND BREAKDOWN ON STOKES-EINSTEIN RELATION IN THE SUPERCOOLED LIQUID STATE OF Zr-Ti-Cu-Ni-Be ALLOYS

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ABSTRACT

Be diffusivity data in the bulk metallic glass forming alloys $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ and $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ are reported for temperatures between 530K and 710K, extending up to 80K into the supercooled liquid states of the alloys. At the glass transition temperature, T_g, a change in temperature dependence of the data is observed in both alloys, and above T_g the diffusivity increases faster with temperature than below. The data in the supercooled liquid can be described by a modified Arrhenius expression containing the communal entropy of the supercooled liquid and based on a diffusion mechanism suggested earlier. The comparison with viscosity data in the supercooled liquid state of $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ reveals a breakdown of the Stokes- Einstein relation, whereas D(T) and η(T) follow a relation close to van den Beukel's. The breakdown of the Stokes- Einstein relation indicates a cooperative diffusion mechanism in the supercooled liquid state of the ZrTiCuNiBe alloys.

INTRODUCTION

Recent investigations of multicomponent deep eutectic metallic systems have led to the development of bulk metallic glasses [1-5] with superior glass forming abilities and an excellent stability with respect to crystallization. This has opened new opportunities for fundamental study of the supercooled liquid state above the glass transition temperature, T_g, as well as of the glass transition in metallic systems, which both were experimentally almost inaccessible before.

For the ZrTiCuNiBe alloy system [4] atomic diffusion [6-8] and viscosity [9], the time-temperature-transformation (TTT) diagram for nucleation and growth of crystals [10] and other thermophysical properties [11] of the supercooled melt have already been investigated. Studies of crystallization in the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy around T_g reveal that crystallization is preceded by phase separation [12, 13]. Further, the availability of bulk specimens has made possible serious mechanical testing which demonstrates that the new alloys are very promising for engineering applications, even more as they can easily be processed and formed in the supercooled liquid state.

This paper reports investigations of atomic diffusion in the glassy and supercooled liquid states of the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (V1) [6, 7] and $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ (V4) [8] alloys, using Be as the diffusing species. Consequences of phase separation for these and other investigations of the supercooled liquid state of V1 are briefly discussed, and diffusivity, entropy and viscosity data are compared with regard to the diffusion mechanism in the supercooled liquid state of these metallic alloys.

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EXPERIMENT

Experimental details of sample preparation and Be diffusion profile measurements by high energy backscattering spectrometry have been given before [6, 14]. In the course of our investigations the onset of a time dependence of diffusivity values after increased annealing times became obvious. This observation initiated more detailed small angle neutron scattering studies of the thermal stability of V1 during isothermal annealing near the glass transition temperature [12, 13], revealing phase separation followed by nanocrystallization. Isothermal annealing of the samples thus must be restricted to the early stages of phase separation where the composition changes grow very slowly and the system stays almost homogeneous. In case of fast Be diffusion we were able to apply annealing times short enough to avoid influence of decomposition and long enough to produce measurable diffusion profiles (Fig. 1). However, investigations on diffusion of the slower diffusors Co and Al in V1 show a decrease of diffusivity with time [15]. In general, one must consider possible influence of compositional changes due to phase separation in ZrTiCuNiBe and other multicomponent glass forming alloys during all isothermal experiments around the glass transition temperature.

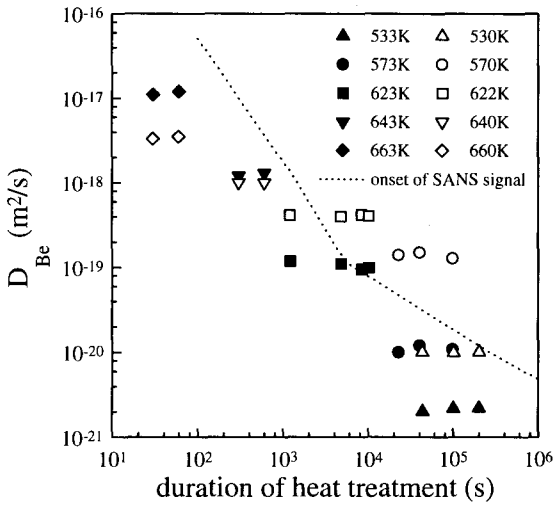

Fig. 1:

Self diffusivity of beryllium in V1 (solid symbols) and V4 (open symbols) as a function of annealing time. The dotted line indicates onset of decomposition in V1, as revealed by small angle neutron scattering (SANS).

RESULTS AND DISCUSSION

In rapidly quenched conventional metallic glasses diffusion is known to be sensitive to the relaxation state of the samples. In a nonrelaxed sample diffusivity drops as a function of time due to structural relaxation and annealing of excess free volume. It approaches a constant value when the sample is fully relaxed. It is thus essential to check for relaxation effects in evaluating diffusion data. As shown in Fig. 1 no dependence of Be diffusivity on the duration of heat treatment could be found within the experimental time-temperature window in both alloys. This ensures that no significant relaxation effects occur. At 623K annealing times ex-

ceeding the early stages of decomposition have been applied to V1, but no significant influence of decomposition on Be diffusivity is visible.

Figure 2 shows an Arrhenius plot of Be diffusivity in V1 and V4. For both alloys, the respective data can be divided into two subsets. The subsets for temperatures below about 625K fit an Arrhenius law $D_{Be}(T)=D_0 \times \exp(-Q/k_BT)$ with $D_0=1.8\times10^{-11}m^2/s$ and Q=1.05eV (V1) and $D_0=8\times10^{-10}m^2/s$ and Q=1.1eV (V4), respectively. Above 625K an enhanced temperature dependence of D_{Be} is observed in both alloys. If interpreted in terms of Arrhenius behavior, this leads to higher activation energies of 4.47eV (V1) and 1.9eV (V4), and to much higher D_0 values of $1.1\times10^{17}m^2/s$ (V1) and $1.7\times10^{3}m^2/s$ (V4).

The change in temperature dependence is associated with the glass transition which in both alloys occurs at about 625K for isothermal annealing experiments. The present data extend 40K into the supercooled liquid state of V1 and 80K into that of V4. This again demonstrates that V4 is more stable against phase separation and crystallization than V1.

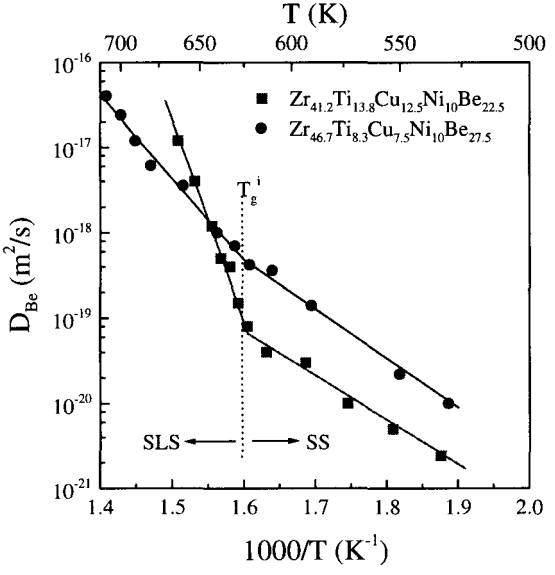

Fig.2:

Arrhenius plot of Be diffusivity in V1 and V4. T_g^i is the glass transition temperature for isothermal annealing. The solid lines represent best Arrhenius fits to the data. The fitting parameters are given in the text.

The small D_0 and Q values for Be diffusion in the solid states of both alloys suggest single atomic jumps of the small Be atoms in the amorphous matrix. The about one order of magnitude higher diffusivity in the solid state of V4 indicates a higher fraction of free volume in this alloy, in accordance with the higher average atomic size in V4 [8]. In the supercooled liquid states (SLS) of both alloys the Arrhenius parameters show increased values. Particularly for V1 the respective numbers seem unphysically high. This indicates that interpretation of the data in the SLS in terms of thermally activated single atomic jumps is not appropriate and a different diffusion mechanism must be involved. We have suggested that diffusion of Be (and probably of other small atoms) in the SLS can be explained by single atomic jumps of the diffusing atoms in a slowly changing configuration of neighboring atoms [6]. The continuous atomic rearrangements in the SLS support the atomic jumps by providing a higher frequency of critical free volume fluctuations. The respective contribution to Be diffusivity is related to the configura-

tional entropy of the supercooled liquid. By taking into account the temperature dependent entropy change $\Delta S^{SLS}(T)$ due to the glass transition, the data can be fitted by the following modified Arrhenius expression:

$$D^{SLS}(T) = D_0^{SS} \cdot \exp\left(-\frac{\Delta H_M^{SS}}{k_B T}\right) \cdot \exp\left(\frac{\frac{N}{N_A} \cdot \Delta S^{SLS}(T)}{k_B}\right),$$

where D_0^{SS} and ΔH^{SS} are the preexponential factor and migration enthalpy for diffusion in the solid state, N is a typical number of neighbor atoms supporting the single jumps by viscous rearrangements, and $\Delta S^{SLS}(T)$ is the temperature dependent configurational entropy per mole of the supercooled liquid. Only the fraction N/N_A of the total configurational entropy which is related to the rearrangements of N nearest and next-nearest neighbor atoms is considered in this expression. Near the glass transition temperature, T_g, the entropy can be approximated by a linear expression, $\Delta S^{SLS}(T) \approx \Delta c_p(T_g) \times (T-T_g) / T_g$, with $\Delta c_p(T_g)$ the specific heat capacity difference at T_g of the supercooled liquid and crystalline states. Figure 3 shows that this expression fits the Be diffusion data of both alloys if one takes N=22 for V1 and N=13 for V4, respectively. For V1 the fit is based on the fully experimentally determined entropy function [11], in the case of V4 it is based on the linear approximation. Beryllium diffusivity in the SLS of the ZrTiCuNiBe alloys scales with the slope of the entropy function above T_g, and the large activation energies above T_g are mimicked by the increase of configurational entropy with temperature. Since $\Delta c_p(T_g)$ is by 2.9 smaller in V4 than in V1 [8], the slope of the entropy vs. temperature function of V4 is smaller and the change in temperature dependence of $D_{Be}(T)$ is less. The smaller number of neighbor atoms involved in Be diffusion in V4 again points to a higher fraction of free volume in this alloy. The change in temperature dependence at T_g with decreasing temperature is related to the rapidly increasing viscosity of the system: below T_g mainly single atomic jumps contribute to diffusion, above T_g cooperative atomic rearrangements dominate the scenario. This change of diffusion mechanism at T_g should only occur for atoms that are able to perform single atomic jumps. Ni diffusivity in $Zr_{55}Al_{10}Ni_{10}Cu_{25}$ also shows a distinct increase in temperature dependence above T_g [16], and data in [17] indicate a small increase in temperature dependence at T_g of Ni diffusivity in V1. No effect is observed for Co diffusion in V1 and Co and Al diffusion in V4 [15], the Arrhenius parameters being comparable to those of Be in the SLS.

The present diffusivity data and the equilibrium viscosity data of V4 in the SLS [9] overlap in the temperature regime 650-710K. Thus, we can check both, the Stokes-Einstein relation [18] and van den Beukel's relation [19], for atomic transport in the SLS of V4 at these temperatures. Figure 4 shows our measured data in the SLS of V4 and the diffusivity as predicted by the Stokes-Einstein relation for translational diffusion, $D(T)=k_BT/6\pi\times\eta(T)\times R$, by choosing the atomic radius of Be, 1.1Å, for the molecular radius R and using the calculated $\eta(T)$ from the Vogel-Fulcher fit to the experimentally determined viscosity. According to Fig. 4, the Be diffusion is much faster in comparison to the prediction of the Stokes-Einstein relation. We believe that the observed breakdown of the Stokes-Einstein relation is another indication for the proposed cooperative diffusion mechanism [6] in the SLS of ZrTiCuNiBe bulk glass formers [8].

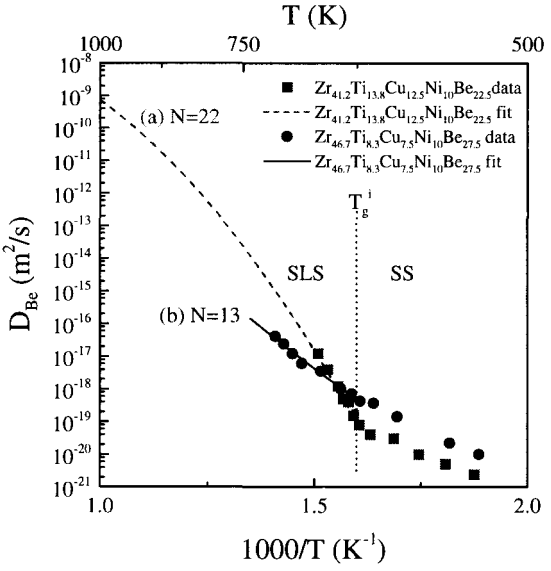

Fig. 3:

D_{Be} data and fit curves to the modified Arrhenius law for data in the supercooled liquid. The fit for V1 is based on the fully experimentally determined entropy function [11], the fit for V4 is based on a linear approximation of the entropy function.

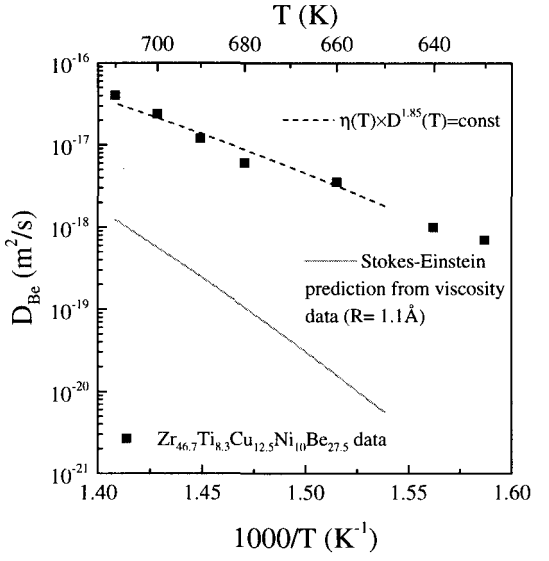

Fig. 4:

Stokes-Einstein prediction for diffusivity (R=1.1Å), as calculated from the Vogel-Fulcher fit for V4 viscosity data [9] (solid line) and result of a fitting procedure of $\eta(D/m^2s^{-1})^n$=const to the data (dashed line, n=1.85, const=3.8×10^{-13}poise).

Based on D(T) and η(T) measurements on conventional metallic glasses, van den Beukel suggested the relation $\eta \times D^2$=const for the correlation of diffusivity and viscosity data [19]. In terms of the free volume model it can be derived by assuming two different defect types with different concentrations responsible for diffusion and viscosity. The present data on V4 follow a relation $\eta \times D^{1.85}$=const which is close to van den Beukel's suggestion (Fig. 4). The interpretation of this experimentally found relation needs to be clarified.

ACKNOWLEDGMENTS

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